

**Lecture 5:** The importance of the reaction medium. Refer to earlier acid/base discussion. Solvent effects on neutral and charged species, ability to promote ionisation, counterions. Reactive intermediates:  $C^-$ ,  $C^\cdot$ ,  $C^+$ . A unified approach to mechanism. Real examples to illustrate  $[A^+ + B^-]$  (neutralisation) and its exact reverse (ionisation) leads to  $S_N1$ . Generalise  $[A^+ + B:]$  &  $[A + B^-]$  etc leads to 1,2-addition to  $C=O$  and b-elimination ( $E1cB$ ,  $E2$ ). Extension of this leads to  $S_N2$ . MO discussion as appropriate.

### **Reactive Intermediates:**

Carbocations

Carbanions

Radicals

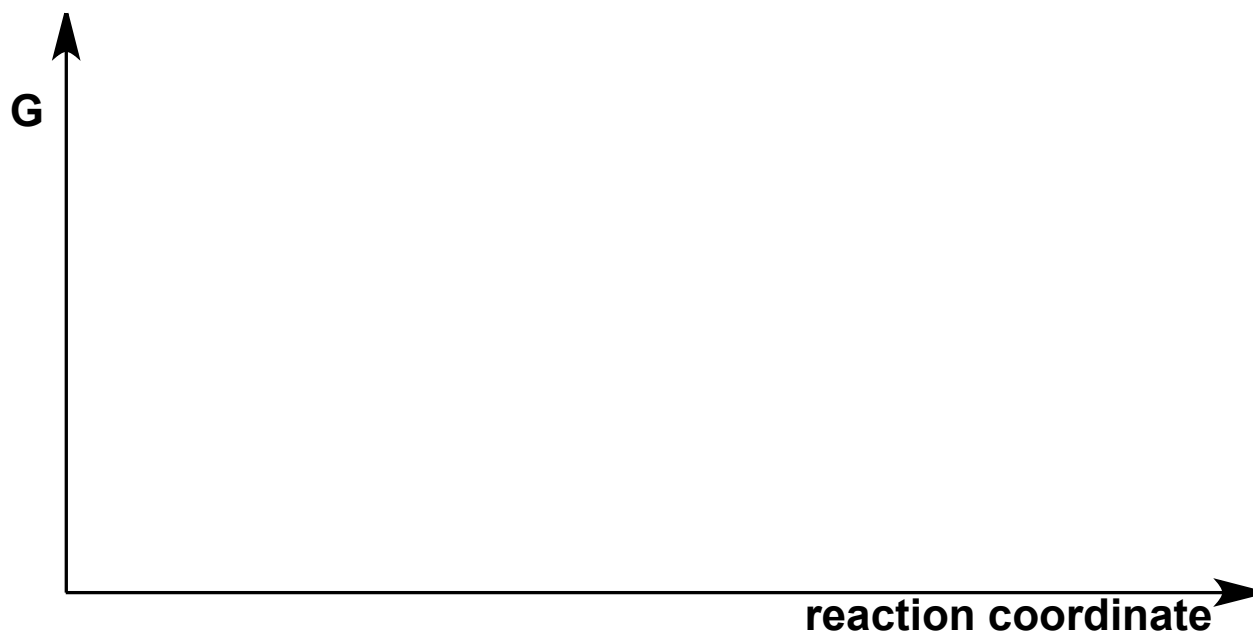
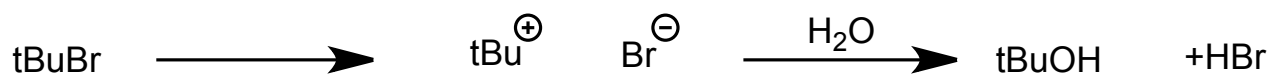
Orbitals and Mechanism 1

Carbenes

## **Solvent Effects on Reactivity**

Acidity/basicity

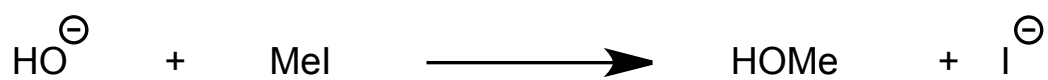
Ionization of alkyl halides



**Curly arrow mechanism:**

**The S<sub>N</sub>1 rate equation:**  $rate = k [\text{tBuBr}]$

i.e. the nucleophile does not contribute towards the rate. Carbocation stability is key.



Curly arrow mechanism:

**The S<sub>N</sub>2 rate equation:**  $rate = k [OH^-][MeI]$

Rate depends on both nucleophile and electrophile.

Structure

Type

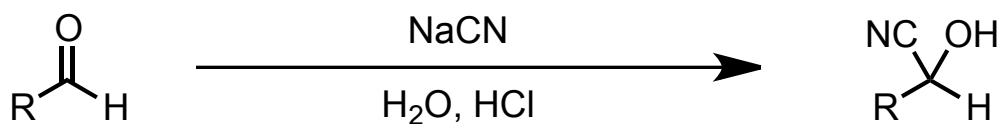
---

S<sub>N</sub>1 reaction?

S<sub>N</sub>2 reaction?

---

**Nucleophilic attack at unsaturated carbon:**



**Lecture 6:** The case of B: = an alkene. Electrophilic addition with  $H^+$  giving a cation leads to discussion of cation structure, stabilisation & regiochemistry. Hyperconjugation. Exact reverse leads to E1 mechanism.  $El^+$  where El bears a lone pair (El = Cl, Br, I) leads to bridged ions and directionality in their opening, stereospecificity.

**Elimination from alkenes:** like nucleophilic substitutions, eliminations may be either first or second order.

**E1 elimination:**

Compare with the nucleophilic substitution of tBuOH with HBr ( $S_N1$ )

What happens when there is no nucleophile present (E1)?

E1 reactions can be *regioselective*:

E1 reactions can be *stereoselective*:

**E2 elimination:**

Compare with the nucleophilic substitution of R-CH<sub>2</sub>Br with OH<sup>-</sup> (S<sub>N</sub>2)

What happens when the nucleophile is made more bulky (E2)?

E2 eliminations are *stereospecific*:

Anion-stabilizing groups allow another mechanism, E1cB:

What factors favour elimination over substitution?



**Electrophilic addition to alkenes:**

Alkenes react with  $H^+$  to give a carbocation

Reaction with HBr is the exact reverse of an E1-type mechanism:

Electrophilic addition to unsymmetrical alkenes may be *regioselective*:

Electrophilic addition of Br<sub>2</sub> to alkenes proceeds via bromonium ions: